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Plasma Chloriding of Thin-Film Silver

A Novel Process in Silver-Silver Chloride Reference Electrode Fabrication

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Silver thin films were modified using a novel plasma modification process for the development of thin-film silver-silver chloride reference electrodes. The surface, physical, and electrochemical properties of these electrodes were investigated by atomic force microscopy, thickness and resistivity measurement techniques, as well as impedance spectroscopy and potentiometry. After plasma treatment, thin-film growth was observed and the electrodes, in general, exhibited low interface impedance and a roughened surface. Evidence of a complex surface reorganization was found. Correlating plasma conditions with film properties suggested that increasing pressure and exposure duration increased species availability, therefore governing the reaction rates, while input power appeared to influence the type of surface chemical reactions. Results also indicated that Ar/Cl₂ mixtures should be employed rather than pure chlorine plasmas.

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Potentiometric sensors are electrochemical devices which find widespread application in, for example, biomedical sensors, water treatment, food, concrete, and metal corrosion assessments.¹ Such sensor systems require the use of a reference electrode, as the signal output is a measured variation of a potential difference and one frequently used reference electrode is based on silver/silver chloride (Ag/AgCl). The effective operation of this electrode relies on the specific electrochemical characteristics of silver chloride, more particularly on its low electrode/electrolyte interface impedance and its stable potential. The fabrication of planar Ag/AgCl electrodes is usually achieved by screen printing silver-loaded inks followed by chemical chloriding² or electrochemical chloriding.³ The addition of chlorine to a silver compound electrochemically "activates" it. This activation can be viewed, in simple terms, as an increase in the number of sites ("active sites") at the surface where little energy is required to exchange charges between the electrode and electrolyte,⁴ thus leading to a lower interface impedance. In order to develop miniaturized sensors based on Ag/AgCl reference electrodes, or microsensor arrays, a thin-film approach is required. Difficulties in manufacturing thin-film Ag/AgCl have been experienced as electrochemical chloriding of such films can lead to their destruction. Limited attempts at direct vacuum deposition of AgCl or chemical chloriding of thin-film silver have proved unsatisfactory.⁵ Indeed, chemical chloriding of thin films offers very restricted process control and has been shown to be surface limited, while deposition under vacuum of AgCl barely achieved the required low interface impedance, nor the essential electrode potential stability.

Chlorine-based plasmas⁶ are widely used in thin-film and semiconductor materials etching.⁷ The research that has been undertaken has concentrated on material etching⁸ rather than film formation, and there has been little work carried out in the modeling of plasma surface reactions due to their complexity and the very limited availability of data from within the plasma.⁹ More recently there have been attempts to understand and control the chlorine plasma chemistry, making sensitive modification of surfaces a possibility.¹⁰ A process based on the use of chlorine plasma techniques, as an alternative to chemical/electrochemical techniques for partial surface conversion of thin-film Ag to AgCl, was recently investigated.¹¹ This preliminary work, based on a capacitively coupled plasma (CCP) reactor, showed the possibility of thin-film Ag chloriding. Auger electron spectroscopy (AES) measurements showed that a complex form of silver chloride (Ag_xCl_y) was formed to depths of at least 50

nm, depending on the plasma parameters. In this work, the silver thin films were processed using an inductively coupled plasma system (ICP), as this plasma configuration offers separate control of the dc bias at the substrate, unlike a CCP system. This is of importance since low-energy processes are required to promote Ag surface modification, without causing significant etching. This paper presents the surface and electrochemical characterization of Ag/AgCl thin-film electrodes created via chlorine plasma treatments. Possible correlation between these characteristics and the plasma parameters are analyzed.

Experimental

A custom-designed ICP system was employed in this study, with power coupled through the top electrode, a flat copper coil, which was driven at 14.0 MHz. The samples were placed on the bottom electrode held at ground potential. The plasma conditions applied were as follows: 10–80 mTorr, 5–50% Cl₂-Ar mixtures or 100% chlorine, at 5–80 W input power, for 10–360 s. Before and after processing, sample thickness, surface topography, and resistivity were determined using a step profiler (Rank Talyor-Hobson Talystep 2010), an atomic force microscope (AFM contact mode, Burleigh SPM 3000), and a four-point probe device (FPP), respectively. To account for possible disparities in the initial silver film thickness, the relative thickness ratio, defined as $(d_{\text{final}} - d_{\text{initial}})/d_{\text{initial}}$, was employed to compare film thickness after processing. Electrochemical characteristics of the untreated and plasma-processed Ag/AgCl thin films were assessed by impedance spectroscopy and potentiometry (Autolab PGSTAT 20 and FRA2, EcoChemie) in a phosphate buffer solution (PBS) to which 0.9% NaCl was added. All impedance measurements were performed using a 10 mV perturbation signal for a frequency window ranging from 10 kHz to 0.1 Hz. The electrode/electrolyte interface can be represented by an equivalent circuit of a resistance (R_{CT}) in parallel with a complex pseudocapacitance¹² (Z_{CPA}), and impedance data when plotted on the complex plane, Fig. 1, usually results in a semicircular plot.¹³ In this paper, except where explicitly stated otherwise, the term impedance refers to the magnitude of the impedance. Reduction of the AgCl formed after each plasma treatment was achieved by applying a linear potential sweep toward negative potential (−0.8 V) at a scan rate of 25 mV/s, starting at the open circuit potential (OCP). This technique was employed to determine the quantity of chlorine added to the thin film and to eventually identify possible differences in the stoichiometry of plasma-processed silver chloride.

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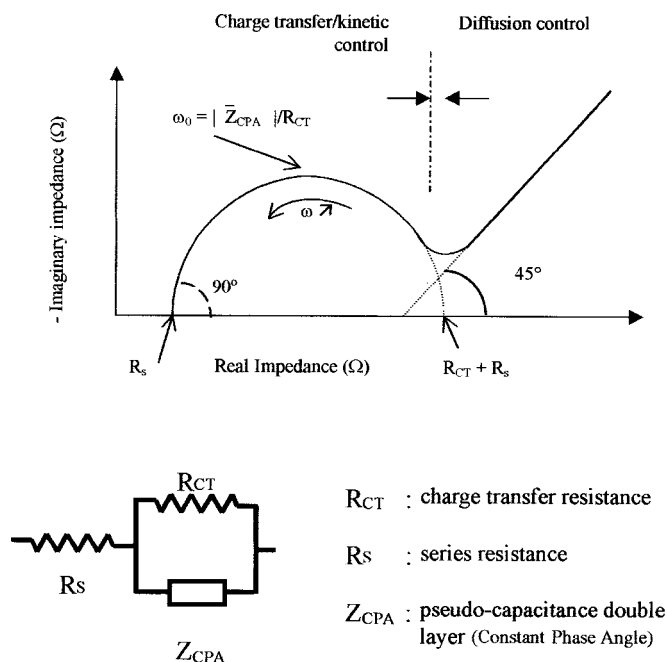


Figure 1. Impedance locus and the electrical equivalent circuit of an electrode/electrolyte interface.

Results

After deposition, Ag thin films exhibited a very smooth surface, Fig. 2a, while a rough topography was observed following plasma processing, Fig. 2b, characterized by numerous islands with density and size variation depending on plasma conditions. Overall, the sample thickness increased with little etching observed, except for samples treated at low Cl_2 fractions (5%) or high input power (80 W). Similarly, the thin-film sheet resistivity increased slightly after plasma treatment, except for 100% Cl_2 where a drastic increase of three orders of magnitude was observed. Both resistivity and thickness measurements showed a correlation with impedance measurements. When plotting resistivity against the magnitude of the impedance, across all process conditions, Fig. 3a, two regimes can be observed. For low impedance, the resistivity is low and tends to increase as the impedance decreases (see inset). In the second regime, the resistivity is initially low but increases as impedance increases (right arrow), ultimately reaching very high values. Figure 3b shows an example of impedance against the corresponding sample relative thickness ratio. Samples treated with a process that achieved low impedance had a wide range of relative thickness ratios from 0 to 1.0; however, high impedance samples showed little film growth with relative thickness ratios around 0.2, suggesting limited chloride formation. Note that film thickness reduction, *i.e.*, etching was rarely observed.

After plasma processing, the impedance of modified Ag thin films was dramatically reduced and the impedance locus exhibited a slightly depressed semicircle, Fig. 4b. Both shape and magnitude differ greatly from that of pure silver, Fig. 4a, which is characterized by a large interface impedance, giving rise to a partial semicircle of large curvature radius. The measured impedance magnitude was plotted against processing time, input power, and pressure for various chlorine fractions, Fig. 5a-c. In all cases, the exposure to Cl_2 or Ar/Cl_2 plasmas reduced the impedance, even after a brief exposure period. The time required to reach an impedance minimum is Cl_2 -fraction dependent and the actual value decreases with increasing fraction. Between 20 and 50% Cl_2 , little difference in the impedance minimum can be observed. At 100% Cl_2 , however, the impedance increases after 1 min plasma treatment, giving a U-shaped impedance-time characteristic, Fig. 5a. Similar behavior

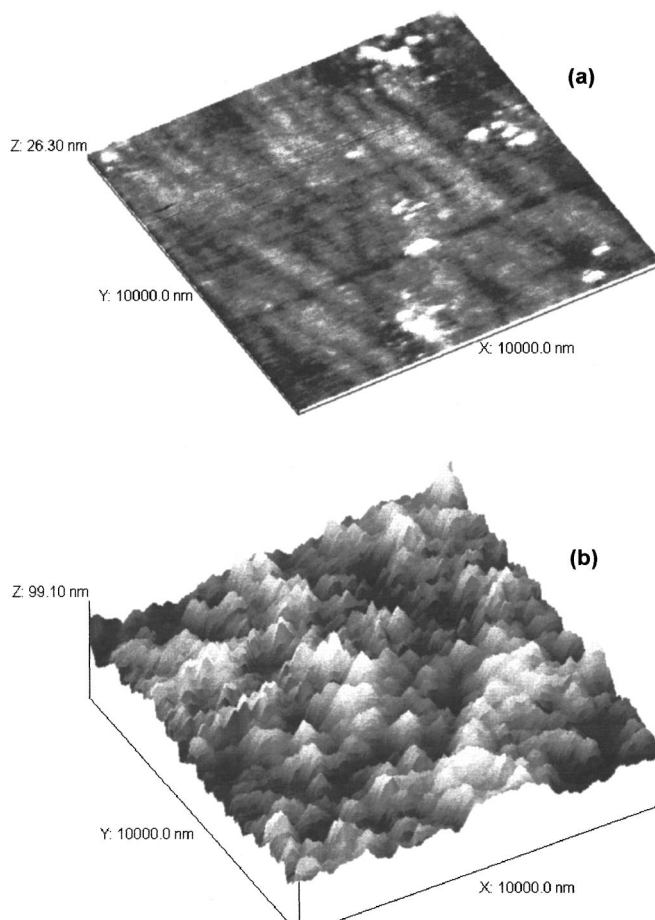


Figure 2. AFM view ($10 \times 10 \mu\text{m}$) of (a) untreated Ag thin film and (b) thin-film Ag plasma-treated at 40 W, 40 mTorr, 20% Cl_2 for 360 s.

was observed while chloriding bulk Ag metal substrates¹⁴⁻¹⁶ and is attributed to an excessive conversion of Ag into AgCl . For low impedance an optimal mixture of metal and chloride is required. Figure 5b shows the fall in impedance with increasing pressure, the rate of decrease being more significant at higher Cl_2 fractions. Similar characteristics were observed with input power, Fig. 5c, the impedance falling rapidly once the power is increased. As with pressure, the impedance minimum depends on chlorine fraction, *i.e.*, the higher the chlorine fraction, the lower the impedance.

Processed thin films were reduced by potentiometry and these samples exhibited reduction peaks, whereas the reduction of pure Ag thin films did not. In the latter case, no current flowed through the interface, indicating that the peaks observed after plasma modification were peaks due to the evolution of silver from an oxidized state to a reduced one, *i.e.*, due to the reduction of AgCl . From the integration of the potentiometric curves, the reduction peak area can be used to estimate the quantity of charge transferred to the thin-film surface. Using this method the charge transfer was observed to increase with pressure and processing time. The maximum estimated transfer was approximately 1000 C/cm^2 . Reduction peaks were observed at potentials similar to those previously noted for plasma-processed thin-film Ag¹¹ while the number of peaks depended on the input power and chlorine fraction. At low input powers ($\leq 20 \text{ W}$), a single narrow peak, at about -0.155 V , was observed, while at higher input powers and for all the other combinations of plasma conditions, a second reduction peak appeared around -0.4 V , Fig. 6. For these double-peaked plots, the more significant peak was narrow and occurred between -0.11 and -0.16 V , with the potential tending toward more negative values with increasing pressure and time.

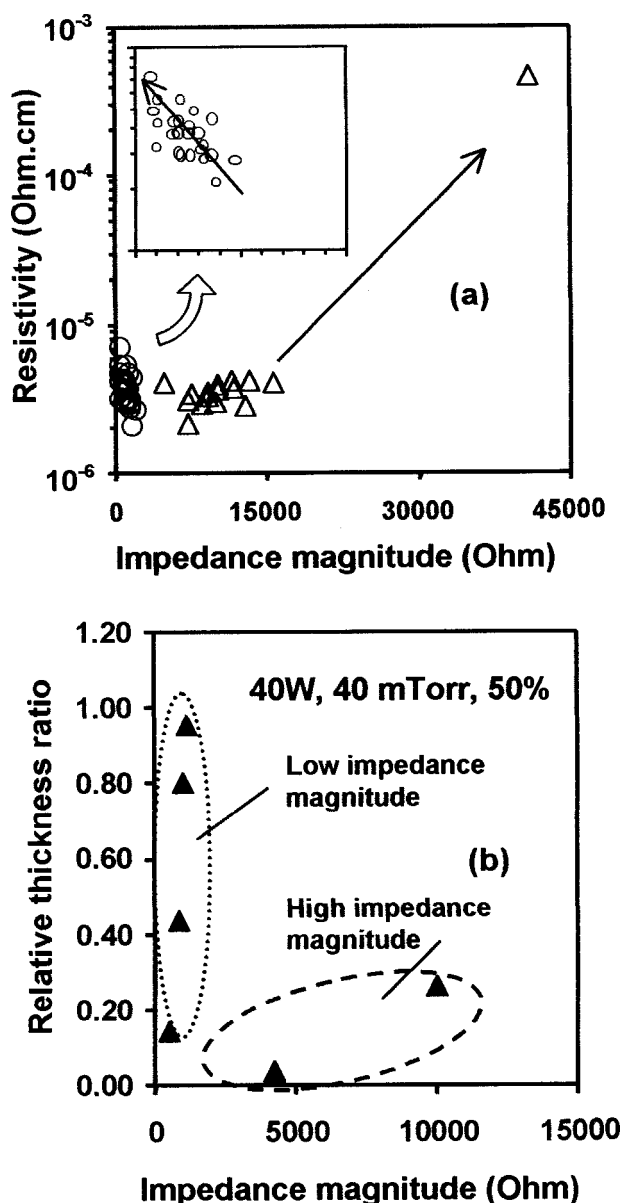


Figure 3. (a) Resistivity against impedance, across various process conditions, and (b) relative thickness ratio ($I - I_0/I_0$) against impedance, for samples processed at 40 W, 40 mTorr, 50% Cl_2 , for 10-360 s.

The second smaller peak was less well defined, appearing at about -0.35 to -0.43 V. An increase in power and/or chlorine fraction shifted the second peak toward potentials of about -0.37 V, regardless of pressure. Figure 7 shows the impedance against the position of the corresponding reduction peak for samples treated for 120 s. No direct correlation could be identified between sample impedance and the first peak potential value. However, it appeared that for the lowest impedance values the second reduction peak had a potential value lying in the narrow range -0.365 to -0.39 V.

Discussion

The first surface assessments indicated that no significant etching was observed and, in fact, the increase in film thickness after plasma processing can be attributed to the conversion of Ag to AgCl^{11} via a reorganization and enlargement of the silver lattice to include chlorine.¹⁷ This is in agreement with the roughening of the surface observed by AFM, which shows a disrupted surface leading to island growth. Impedance measurements showed a reduction of the

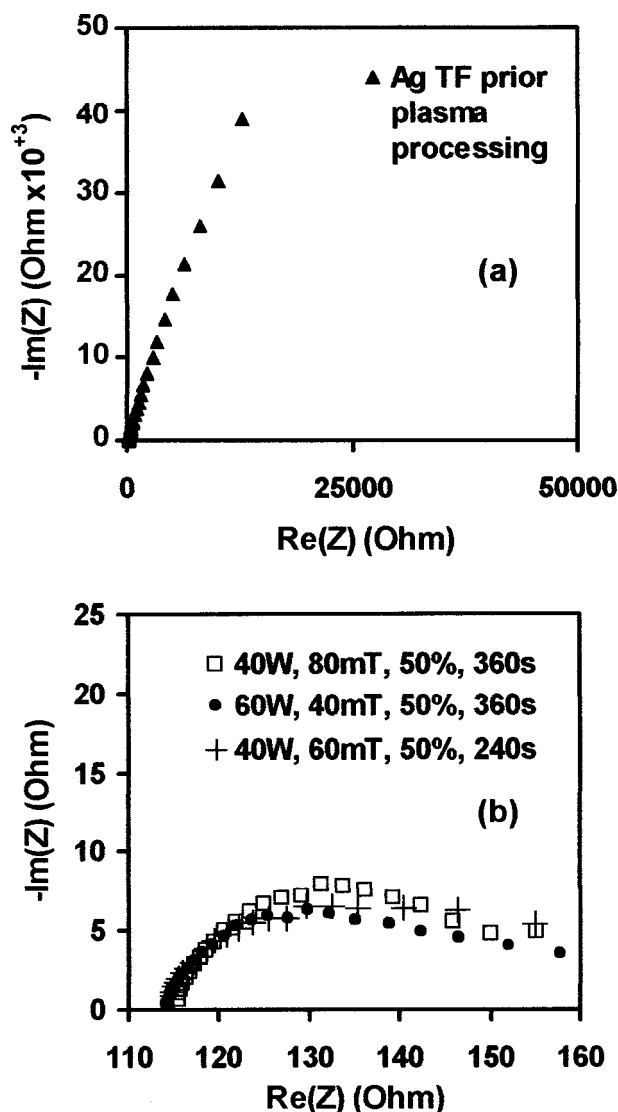


Figure 4. Impedance spectra of (a) pure Ag thin film and (b) typical plasma-treated Ag thin film. Note three orders of magnitude scale difference.

interface impedance due to this addition of AgCl to the surface. Furthermore, the comparison of the impedance loci of pure Ag and plasma-modified Ag, Fig. 4a and b, suggests that the silver surface electrochemical properties are dramatically modified by exposure to the chlorine plasma. The initial silver surface was shown to be very smooth, Fig. 2a, and may be free of active sites, leading to a mainly capacitive interface behavior and hence the large partial semicircle observed, Fig. 3. However, after plasma treatment, the number of active sites at the thin-film surface increased, facilitating the faradaic process of charge transfer, and was observed as a depressed semicircle. This decrease in the impedance locus may also be a consequence of a larger active surface area, as it affects the pseudocapacitance component. The observed depressed semicircle, with an angle lower than 90° , is indicative of a rough surface¹² and corroborates the AFM surface observations, Fig. 2b. The growth of AgCl , an insulator, via conversion of metallic Ag increases the resistivity of the films, Fig. 3a. The correlation of increasing resistivity, thin-film growth, and decreasing impedance, Fig. 3a and b, is further evidence of the lattice disruption due to the chlorine uptake. Although the results obtained so far do not allow speculation on the modified film structure, the observed reduction peaks are further evidence of complex surface reorganization. The two reduction peaks suggest the presence of slightly different stoichiometries, in agreement with the

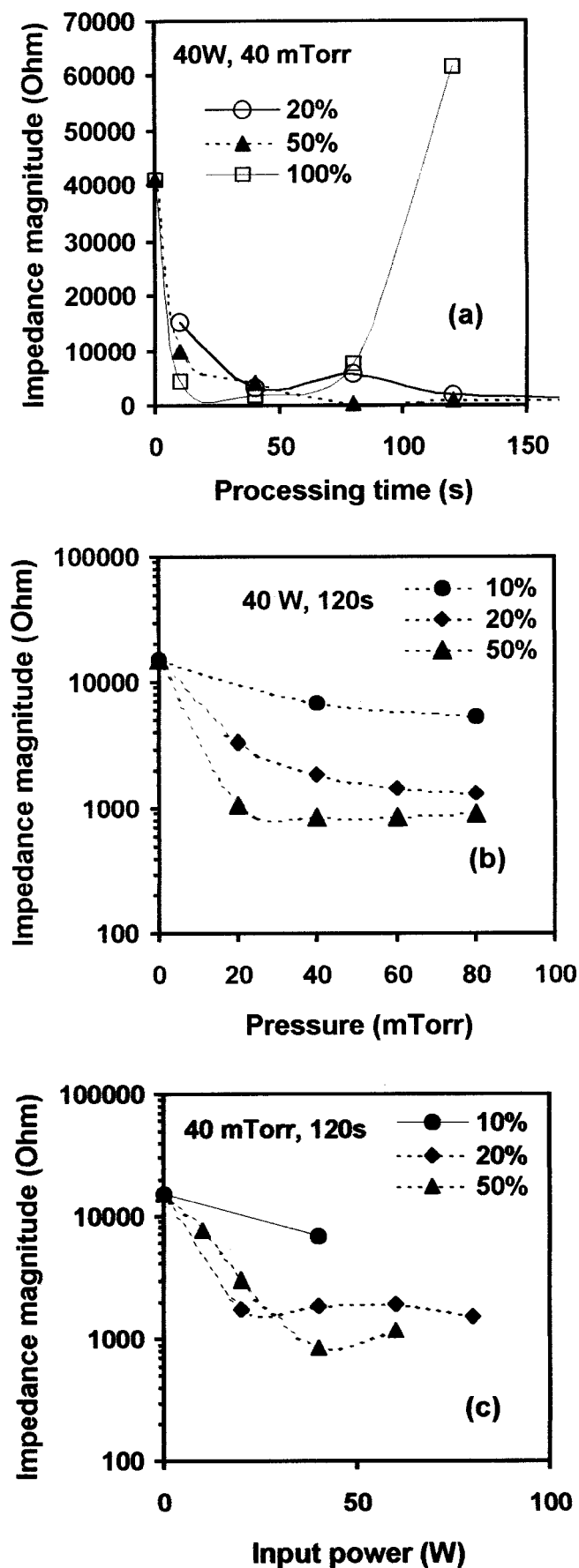


Figure 5. Impedance vs. (a) processing time (40 W, 40 mTorr), (b) pressure (40 W, for 120 s), and (c) input power (40 mTorr, for 120 s).

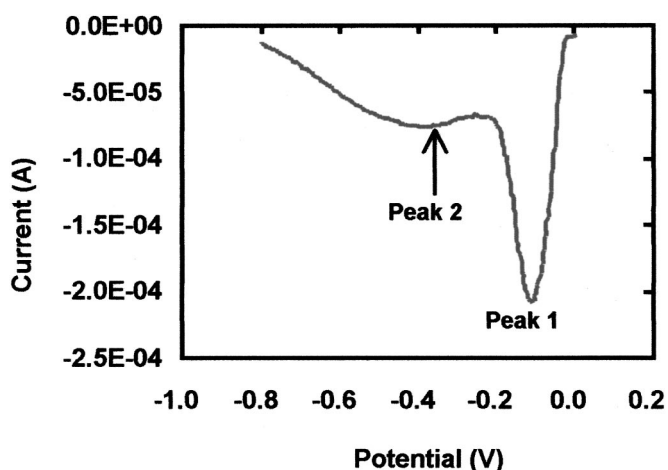


Figure 6. Typical spectrum obtained by linear potential sweep (OCP to -0.8 V) at 25 mV/s scan rate.

nonstoichiometric Ag/Cl ratios found by AES and reported elsewhere.¹¹ Matsunaga *et al.*¹⁷ have shown that several types of nonstoichiometric structure, Ag_xCl_y , can exist due to the possible presence of interstitial Ag as well as cation vacancies,¹⁸ leading to structural flexibility and higher conductivity. However, this plasma-based chloriding technique is a novel process, and a key to further understanding of the surface chemical reaction(s) may be found in the plasma reaction processes themselves.

Many interactions occur in the bulk of the plasma which produce and destroy plasma particles. In particular, argon-chlorine plasmas contain argon neutrals, ions, and excited states, such as metastable, higher state, and resonant species, and chlorine species, namely, Cl_2 , Cl , Cl_2^+ , Cl^+ , Cl^- , and potentially, Cl_2^* and Cl^* .^{9,19} The production/destruction and thus the concentration of each plasma species is directly controlled by the input power, pressure, and chlorine fraction. Preliminary Langmuir probe analysis of the internal plasma conditions indicate that over the range 0-60 W and for Cl_2 fractions higher than 5%, the positive ion density is reasonably constant and independent of pressure.⁹ Laser-induced fluorescence (LIF) also indicated a rise in atomic Cl density following an increase in power and/or pressure. A more detailed presentation of plasma measurements and chemical modeling will be given in a separate paper. Once produced, some of these particles can reach the surface of the thin-film substrate, where physical and chemical reactions are likely to occur with silver atoms.

In simple terms, the present results, as well as results reported elsewhere,²⁰ seem to indicate that increasing power or processing time, beyond a certain point, tended to increase impedance, whereas

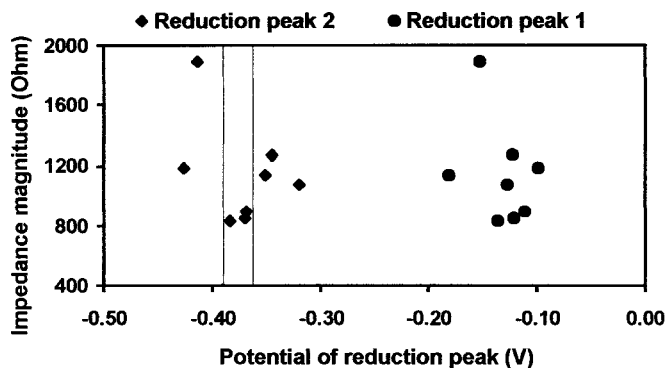


Figure 7. Impedance vs. reduction peak potential for samples treated for 120 s under various plasma conditions.

pressure or chlorine fraction increases had almost the opposite effect. Under these latter conditions, the higher chlorine density within the plasma is thought to lead to increased chlorine species bombardment of the surface, whereas the input power influences, in the main, the species energy.^{9,21} The reduction in impedance and improvement in AgCl formation appear to be a low-energy process with the rate of conversion determined primarily by the concentration of arriving halogen species. The thickness increase with pressure and chlorine fraction increase is also consistent with an increase in reactant species availability at the surface, leading to increased growth and hence, lower impedance. Thus, the number of surface reaction sites may be adequate, but it is the transport of species from the plasma bulk that is the main rate limitation. From this simple picture, one could postulate that a low-power 100% Cl₂ mixture would be optimal, as it was observed that increasing the chlorine fraction led to a sharper drop in impedance. However, the increase in impedance with mixtures of over 50% Cl₂ and with long plasma exposure times suggests a change in the nature of the rate limitation in these regimes. One possibility is the total conversion of the surface to Ag_xCl_y, which would be more likely at very high chlorine densities, since total conversion is known to be detrimental. Also, complete conversion of the surface creates a barrier to further chlorine uptake and film growth.²² Thus, at high Cl₂ fractions, the reaction limitation may be due to a restricted availability of surface reaction sites. Increasing power, as a rule of thumb, generally increases the density²³ and energy of ionic species.²⁴ Over a limited range, increasing power promoted improvement in the interface impedance behavior and AgCl growth, indicating that energetic ionic species do play some role in promoting surface reactions. Surface reaction rates are, however, an extremely complex collection of competing processes.⁸ The fact that different chlorine ions, Cl₂⁺ and Cl⁺, as well as Ar⁺, are involved in the plasma process is consistent with the different Ag_xCl_y stoichiometries identified by potentiometry. First, the difference in potential values of the two reduction peaks, Fig. 6, suggests different bonding energies, as a more negative potential is indicative of a more thermodynamically stable state and thus, a stronger Ag-Cl bond. Second, Langmuir probe results indicate a correlation between total positive chlorine ion concentration (Cl₂⁺ + Cl⁺) and the shift in potential of the second reduction peak, Fig. 7, suggesting that input power does control to some extent the quality of the silver chloride at the surface. Furthermore, continuous inert argon bombardment also impacts on the surface reaction rate by, for example, roughening the surface by sputtering²⁵ or increasing the temperature and affecting surface diffusion. These disruptions could then enhance the creation of active sites and the transport of species through the interfacial AgCl layer.²⁶ Thus, the observed loss of Ar⁺ at higher Cl₂ fractions could be a factor in the observed impedance increase in this regime. However, the positive influence of plasma power, through the creation of energetic species, is restricted by the possibility of etch/sputtering of Ag/AgCl, as evidenced by the reduction in thickness at high input power.

Conclusions

Chlorine plasma modification of thin-film silver has been shown to be a controllable method of fabricating thin-film Ag/AgCl reference electrodes with stable characteristics and low impedance values, suitable for use as a "nonpolarizable" reference electrode. The low impedance occurs as a consequence of a stable Ag_x-Cl_y bond formation and of a roughened surface. The most significant param-

eters in achieving optimal characteristics are the Cl₂ fraction, up to 50%, and the pressure. The conversion rate of native Ag from the surface to Ag_xCl_y depends predominantly on the availability at the surface of halogen reactive species and hence its transport from the plasma bulk. The potentiometric reduction of Ag/AgCl thin films suggests a complex stoichiometry and different bonding arrangements, which may be due to surface bombardment by different halogen species. The surface rearrangement, as deduced from the position of the reduction peaks, showed some correlation with input power. Work is currently in progress to characterize the internal plasma conditions in detail and hopefully provide a further understanding of surface reaction mechanisms and their implications on device performance. Also, the integration of such thin-film electrodes into various device structures and the consequences for reproducibility and device life are being investigated.

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